

Supporting Information for

Local Electronic Structure Changes in

Polycrystalline CdTe with CdCl₂ Treatment and Air

Exposure

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Grain boundary profiles of CdCl₂-treated CdTe

The electronic grain boundary model developed by Seto estimates the net doping density (p_{net}) and grain boundary (GB) trap density ($p_{trap,GB}$) given the depletion width (w) and the magnitude of band bending ($\Delta\Phi_{GB}$) at the space charge region (SCR) near GBs.¹ To perform this analysis, grain boundaries were identified in the vacuum level (E_{vac}) map of CdCl₂-treated CdTe after air exposure.

Grain-to-grain and grain-to-boundary contrast in the ionization energy (IE) and the corresponding maxima in the 1st spatial derivative of IE [$d(IE)/dx$] helped map the location of GBs. This GB map was then overlaid on the E_{vac} map, and the SCRs near GBs were sampled by extracting line profiles oriented approximately orthogonal to grain boundaries, and spaced evenly from one another.

Figures S1a and S1b shows the perimeters of some grains (outlined in yellow) obtained from contrast in the IE map (Figure S1a) and the $d(IE)/dx$ map (Figure S1b) of CdCl₂-treated CdTe after air exposure. The GB map from each image match well. Figure S1c shows the complete GB map that resulted from this procedure, overlaid onto the E_{vac} map of the same location. The locations of E_{vac} line profiles taken along GBs, used to generate fits of the depletion width and barrier height of the space charge region (SCR) near GBs, are shown as blue lines in Figure S1c.

Of the 356 grain boundaries sampled, line profiles were either relatively flat, showed stepwise variation, or showed decrease in E_{vac} . Figure S2a shows examples of relatively flat, stepwise, and decreasing E_{vac} at the grain boundaries. Line profiles that had a decrease (downward band bending) in the E_{vac} at the location of the GB were fit with a Gaussian peak superimposed over a linear background to extract characteristics of the SCR. 172 of 356 grain boundaries exhibited this decrease in E_{vac} and were fitted.

The FWHM of the Gaussian peak corresponded to the depletion width (w) of the SCRs near GBs. The amplitude of the Gaussian peak was associated with the magnitude of band bending at the GB ($\Delta\Phi_{GB}$).

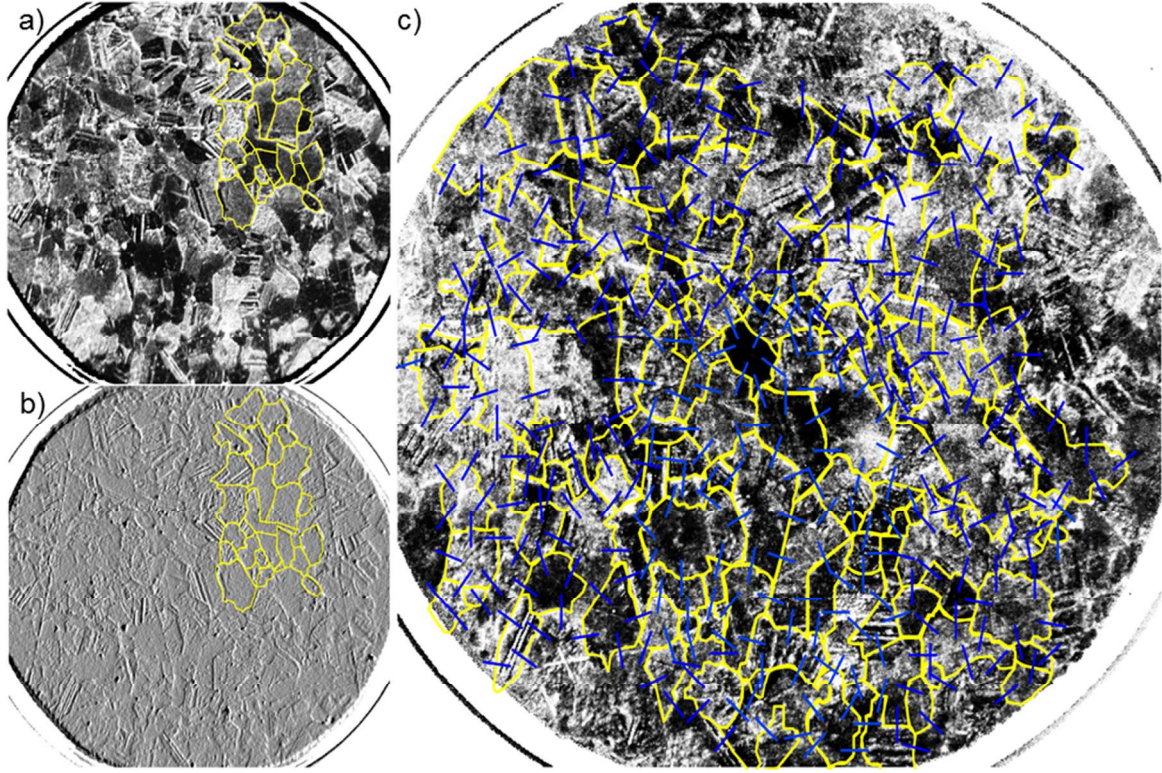


Figure S1. Maps of the (a) ionization energy (IE) and (b) $d(IE)/dx$ of $CdCl_2$ -treated $CdTe$ after air exposure, with some grain domains outlined in yellow. The derivative was taken along the horizontal x direction. (c) Perimeters of identified grains are outlined by yellow lines overlaid on the corresponding vacuum level (E_{vac}) map. The location of line profiles sampled along grain boundaries (GBs) are shown in blue lines. IE and E_{vac} maps were obtained from local measurements of the photoemission threshold and photoemission spectra, respectively. The field of view for maps was $48\ \mu m$.

Figures S2b and S2c show histogram analyses of w and $\Delta\Phi_{GB}$ obtained from the 172 analyzed GBs. The distribution of $\Delta\Phi_{GB}$ is asymmetric about the average value of 70 meV, and has a standard deviation of 30 meV; the distribution of w is asymmetric about the average value of 290 nm, and has a standard deviation of 100 nm. According to the grain boundary model developed by Seto,^{1,2} values of net doping density (p_{net}) and GB trap density ($p_{trap,GB}$) are obtained from w and $\Delta\Phi_{GB}$ using the following expressions:

$$p_{net} = \frac{2\varepsilon\varepsilon_0\Delta\Phi_{GB}}{e^2w^2}, \quad p_{trap,GB} = \frac{1}{e}\sqrt{8\varepsilon_0\varepsilon(p_{net})\Delta\Phi_{GB}},$$

where $\varepsilon = 10.3$ is the dielectric permeability of CdTe,³ ε_0 is the dielectric constant, and e is the elementary charge. These expressions yield $p_{net} \approx 10^{15} \text{ cm}^{-3}$ and $(p_{trap})_{GB} \approx 10^{11} \text{ cm}^{-2}$ for CdTe.

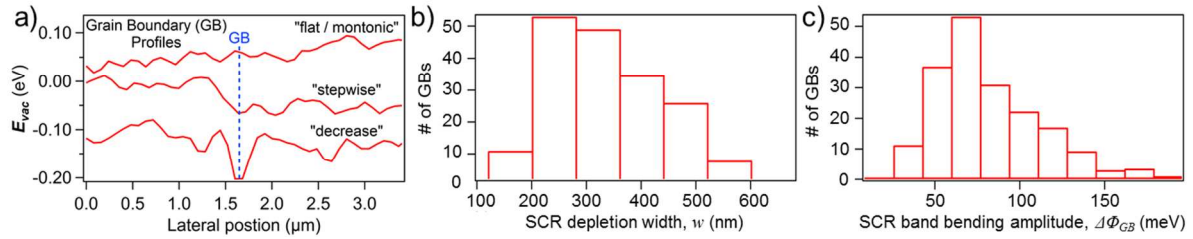


Figure S2. (a) Typical vacuum level variation observed at grain boundaries (GBs), and distributions of (b) the depletion width of the near-GB space charge region (SCR) and (c) the magnitude of band bending for “decreasing” (downward band bending) GBs.

Vacuum level and ionization energy mapping of CdCl₂-treated and untreated CdTe, before and after air exposure

As described in the experimental section and in refs. 4 and 5, local photoemission spectra and the photoemission yield curves provide maps of the relative vacuum level (E_{vac}) and ionization energy (IE). Variation of E_{vac} indicates relative work function variation, assuming Fermi level alignment in the sample. E_{vac} and IE maps for CdCl₂-treated and untreated CdTe, before and after air exposure, are compared in Figure S3.

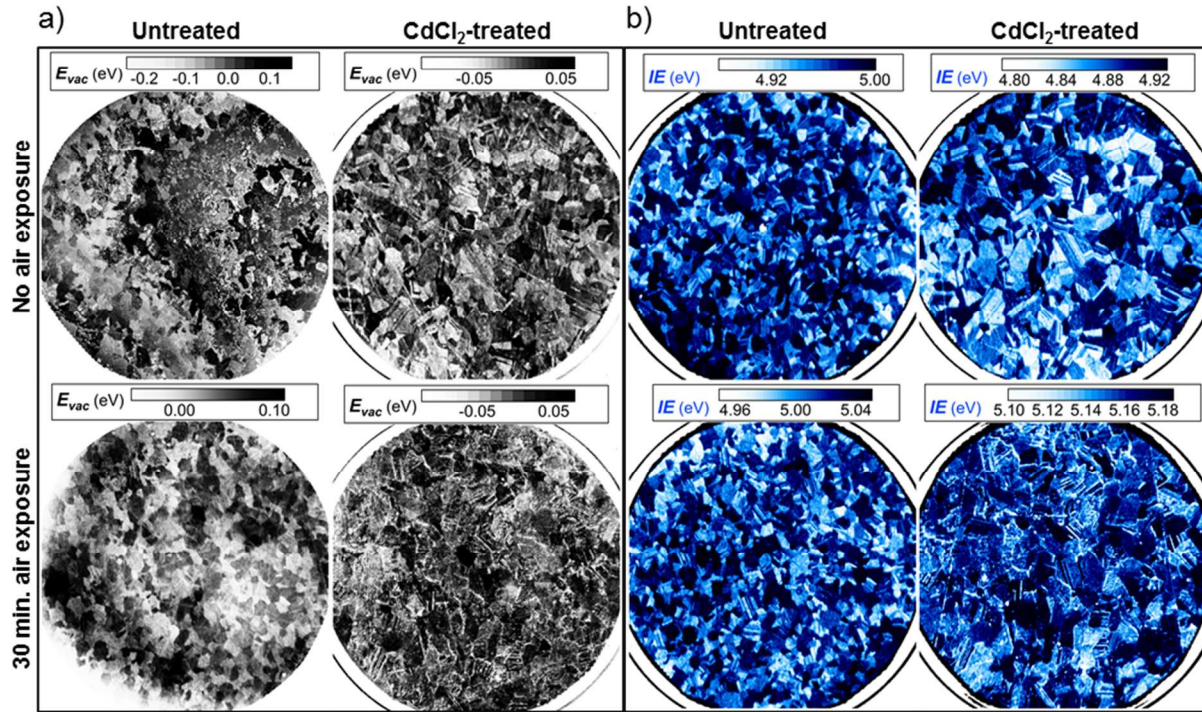


Figure S3. Maps of the (a) vacuum level and (b) ionization energy of untreated and CdCl₂-treated CdTe, before (top row) and after (bottom row) air exposure. Ionization energy (IE) and vacuum level (E_{vac}) maps were extrapolated from local measurements of the photoemission threshold and photoemission spectra, respectively. PEEM measurements of local photoemission threshold and photoemission spectra are described in ref. 5. Color scales for maps were chosen to highlight grain and grain boundary (GB) contrast. The field of view for maps was 48 μ m.

E_{vac} (Figure S3a) and IE (Figure S3b) maps of untreated CdTe films before and after air exposure show grain-to-grain variation similar to CdCl₂-treated CdTe prior to air exposure. Grain-to-boundary variation of the E_{vac} and IE did not appear in CdTe until the CdCl₂-treated CdTe was exposed to air. E_{vac} maps for CdCl₂-treated and untreated CdTe resembled photoemission intensity images previously reported in ref. 6. Aberrations from an unstable sample/holder contact affected the field distribution in the E_{vac} map of untreated CdTe (Figure S3a, right column), similar to observations in ref. 6.

Histograms of these PEEM spectral maps help quantify and compare the extent of electronic structure variations. Figure S4 shows histograms for E_{vac} (Figure S4a) and IE (Figure S4b) maps in Figure S3. The histograms were fitted using multiple Gaussian functions, denoted by dashed lines and numerical labels in Figure S4. Solid lines in Figure S4 indicate the overall fits.

Comparison of general trends (e.g. number of components, FWHMs) was the aim of this analysis, thus no specific physical parameters were imposed on the fittings. The general procedure for fitting was to include enough Gaussian fit functions to fit the edges of the histogram distribution, then introduce additional fit functions to improve the overall fit, if necessary.

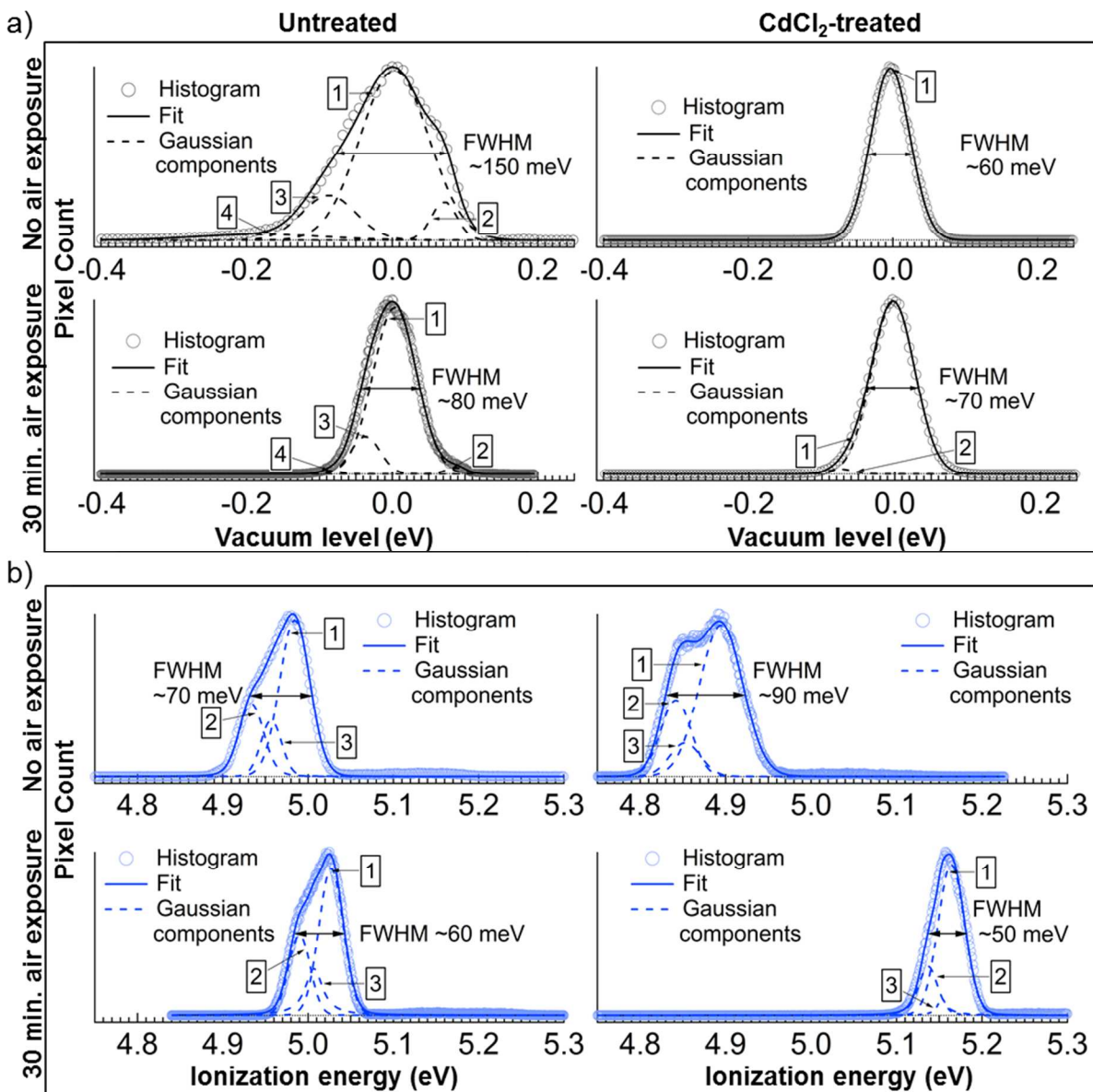


Figure S4. Histograms of (a) E_{vac} and (b) IE obtained from spectral maps of CdTe films with/without CdCl₂ treatment and with/without air exposure shown in Figure S4. Dashed lines with numerical labels indicate independent Gaussian fit functions, and solid lines correspond to the overall fits.

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REFERENCES

- (1) Seto, J. Y. W. The electrical properties of polycrystalline silicon films. *J. Appl. Phys.* **1975**, 46 (12), 5247-5254.
- (2) Sadewasser, S.; Glatzel, Th.; Schuler, S.; Nishiwaki, S.; Kaigawa, R.; Lux-Steiner, M.Ch. Kelvin probe force microscopy for the nano scale characterization of chalcopyrite solar cell materials and devices. *Thin Solid Films* **2003**, 431-432, 257-261.
- (3) Strzalkowski, I.; Joshi, S.; Crowell, C. R. Dielectric constant and its temperature dependence for GaAs, CdTe, and ZnSe. *Appl. Phys. Lett.* **1976**, 28 (6), 350-352.
- (4) Yi, Y.; Lyon, J. E.; Beerbom, M. M.; Schlaf, R. Characterization of indium tin oxide surfaces and interfaces using low intensity x-ray photoemission spectroscopy. *J. of Appl. Phys.* **2006**, 100, 093719.
- (5) Berg, M.; Keyshar, K.; Bilgin, I.; Liu, F.; Yamaguchi, H.; Vajtai, R.; Chan, C.; Gupta, G.; Kar, S.; Ajayan, P.; Ohta, T.; Mohite, A. D. Layer dependence of the electronic band alignment of few-layer MoS₂ on SiO₂ measured using photoemission electron microscopy. *Phys. Rev. B* **2017**, 95, 235406.

(6) Berg, M.; Kephart, J. M.; Sampath, W. S.; Ohta, T.; Chan, C. Effects of CdCl_2 treatment on the local electronic properties of polycrystalline CdTe measured with photoemission electron microscopy. *44th IEEE Phot. Spec. Conf.* **2017** (in press); arXiv 1710.07332 [cond-mat.mtrl-sci].

(7) Vigil-Galán, O.; Vaillant, L.; Mendoza-Pérez, R.; Contreras-Puente, G.; Vidal-Larramendi, J.; Morales-Acevedo, A. Influence of the growth conditions and postdeposition treatments upon the grain boundary barrier height of CdTe thin films deposited by close space vapor transport. *J. Appl. Phys.* **2001**, 90 (7), 3427-3431.